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THE EFFECT OF WATER QUALITY ON THE MERCURY CONCENTRATION OF NORTHERN PIKE (*ESOX LUCIUS*, L.) IN FINNISH FOREST LAKES AND RESERVOIRS

Jaakko Mannio, Matti Verta, Pirkko Kortelainen & Seppo Rekolainen

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Correlations between water quality parameters and the total mercury concentration in northern pike (*Esox lucius* L.) were studied in 35 forest lakes and 10 reservoirs located mainly in Central Finland and Ostrobothnia. The concentrations of mercury in pike (750 g) varied from 0.21 to 1.02 mg kg⁻¹ in lakes and from 0.42 to 1.80 mg kg⁻¹ in reservoirs. All estimates of the content of humic matter in water correlated positively ($P < 0.001$) with the mercury content in pike. Water pH and nutrients were related to the humic matter. In multiple regression analysis other water quality parameters could not explain essentially more the variation of mercury contents in pike. The results support observations that the total input of humic matter from the drainage area appears to contribute to the high concentrations of mercury in pike in headwater lakes. In young reservoirs the dissolved organic matter from inundated soil seems to be the main source of mercury.

Index words: Mercury, water quality, aquatic humus, forest lake, reservoir.

1. INTRODUCTION

Many factors contribute to the variability in the mercury body burden experienced by different organisms. A most important factor is obviously the amount of mercury to which the organism is exposed, i.e. the concentration in ambient water, in sediments and in food. The uptake of mercury by fish is also influenced by several biotic and abiotic factors including fish growth and metabolic rate (Olsson 1976, Rodgers and Beamish 1981), calcium (McFarlane and Franzin 1980, Wren and MacCrimmon 1983), alkalinity (Schnei-

der et al. 1979), pH (Landner and Larsson 1972, Jernelöv et al. 1975, Hultberg 1978, Suns et al. 1980, Wren and McCrimmon 1983), degree of eutrophication (D'Itri et al. 1971, Beijer and Jernelöv 1979) and humus (Hultberg 1978, Björklund 1982). Verta (1981) demonstrated a relationship between mercury in pike and water colour, COD and pH in Finnish reservoirs. Fish in unpolluted areas have also been reported to contain elevated Hg concentrations (D'Itri et al. 1971, Landner and Larsson 1972, Suns et al. 1980, Akielaszek and Haines 1981, Wren and MacCrimmon 1983).

The amount and nature of humic matter in water and sediments and its effect on fish mercury contents are of considerable interest. The possible role of humic substances in the mercury cycle has been suggested by several workers (Hultberg and Hasselrot 1981, Verta 1981, Alfthan et al. 1983). Humic matter is able to complex (e.g. Lindberg and Harris 1974, Beneš et al. 1976) and solubilize mercury (Miller 1975, Gjessing 1976). Abiotic methylation of mercury has also been shown to occur by reaction with humic substances (Rogers 1977, Nagase et al. 1982).

The aim of this study was to determine water quality parameters which can explain the mercury concentrations in northern pike in natural forest lakes and in reservoirs remote from any direct external source of mercury contamination.

2. MATERIALS AND METHODS

2.1 Study area

The lakes of this study were located mainly in headwaters of the water divide area of Central Finland and the reservoirs were located in Ostrobothnia and Lapland (Fig. 1). The lakes and reservoirs represented a relatively wide range of chemical variables such as water colour, pH and total phosphorus (Table 1). The range in physical parameters was also wide: the smallest forest lake had an area of 0.04 km² and the largest 99 km². The area of the largest reservoir, Porttipahta, was 214 km². The hydrography of the forest lake basins has been presented by Verta et al. (1986b) and of the reservoirs by Verta et al. (1986a).

2.2 Water samples

Water samples were taken from a depth of one metre during winter stratification and autumn turnover in 1983. In the case of several of the lakes situated in remote areas only a few previous measurements of water quality were available. Therefore only the 1983 results were used in the correlation analysis.

The concentration of organic matter was measured by several different, independent

methods described in detail by Pennanen et al. (1986). COD_{Mn} and water colour were standard methods (SFS 3036 and SFS 3023 respectively). Absorbance measurements were made of both initial samples and of the fractions obtained by gel chromatography (Sephadex G-100) at a wavelength of 254 nm. Fractions representing colloidal and particulate organic matter (Pennanen 1982, Pennanen et al. 1986) were pooled and are referred to here as the HMW-fraction (high molecular weight organic matter). The HMW-fraction included most of the iron which contributes to the absorbance of the sample (Pennanen 1982). The dissolved fraction was called LMW-fraction (low molecular weight organic matter). Total organic carbon (TOC) and dissolved organic carbon (DOC) analyses were carried out using an infrared gas analyzer (Salonen 1979).

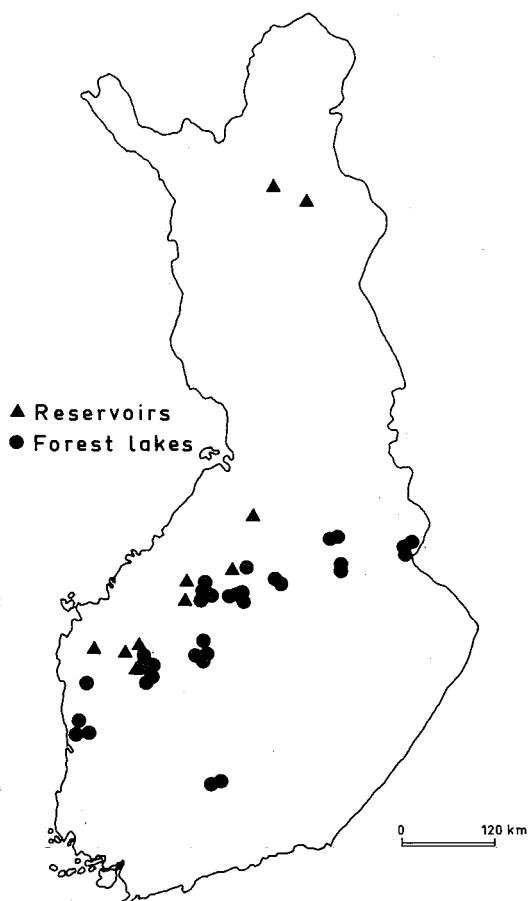


Fig. 1. Study areas.

Table 1. Water chemistry during the autumn overturn of 1983 and mercury contents in 750 g pike (F Hg mg kg⁻¹) in the study lakes and reservoirs. HMW and LMW are gel-fractionated optical estimates of high molecular weight and low molecular weight humic matter concentration.

Study area	Conductivity mS m ⁻¹	Alkalinity mmol l ⁻¹	pH	Colour Pt mg l ⁻¹	COD _{Mn} O ₂ mg l ⁻¹	HMW A254 · 10 ⁻³	LMW A254 · 10 ⁻³	tot P μg l ⁻¹	Fe μg l ⁻¹	F Hg mg kg ⁻¹
Lakes										
Jonkeri	1.8	0.05	6.3	80	12	112	258	12	590	0.38
Saunajärvi	1.9	0.04	6.0	160	19	176	370	26	1400	0.44
Kälkänen	1.8	0.05	6.4	70	10	75	251	12	480	0.45
Jornasjärvi	2.8	0.06	6.4	90	13	106	540	12	282	0.71
Kolmisoppi	2.7	0.03	5.7	180	25	249	527	52	1200	0.89
Älänne	1.8	0.04	6.2	25	7	39	144	22	250	0.29
Tiilikka	1.7	0.02	6.3	90	12	111	237	14	1100	0.51
Sulkavanjärvi	5.0	0.16	7.0	90	14	86	412	33	760	0.52
Rytkynjärvi	5.4	0.18	6.9	100	15	117	370	39	940	0.51
Elämäjärvi	3.3	0.11	6.5	120	17	227	285	49	1600	0.60
Saani järvi	3.8	0.13	6.5	140	17	225	398	55	2000	0.54
Alvajärvi	4.3	0.17	6.8	40	9	31	181	13	190	0.52
Kolima	4.1	0.15	6.9	50	9	28	232	9	220	0.45
Pääjärvi	3.2	0.09	6.4	160	16	308	364	67	2300	0.85
Kimminginjärvi	2.0	0.05	6.3	35	7	34	124	16	220	0.42
Kiesimenjärvi	2.4	0.06	6.3	100	15	143	284	49	810	0.67
Karankajärvi	3.2	0.08	6.2	140	17	213	434	40	1500	0.62
Ylä-Jappajärvi	2.7	0.09	6.4	160	17	361	339	49	2800	1.02
Pihlajavesi	3.0	0.06	6.4	90	13	115	444	17	980	0.86
Salamajärvi	3.5	0.05	6.4	150	12	285	416	16	2500	0.61
Lehtosenjärvi	1.8	0.01	5.4	180	22	283	275	31	2500	0.89
Lestijärvi	2.6	0.06	6.3	85	13	103	323	8	1200	0.21
Parkkimanjärvi	4.2	0.16	7.0	30	10	14	185	7	160	0.45
Seinäjärvi	2.9	0.03	5.9	140	17	239	250	41	1900	0.66
Iso Soukkajärvi	2.8	0.08	6.2	80	19	52	199	41	530	0.49
Kuorasjärvi	3.8	0.04	5.6	90	15	122	286	27	1100	0.52
Jääskän järvi	4.9	0.07	6.0	120	19	229	301	60	1500	0.91
Vetämäjärvi	4.9	0.07	6.1	80	14	61	276	50	600	0.49
Kangasjärvi	2.5	0.00	5.7	10	3	6	17	13	180	0.57
Siikajärvi	6.0	0.12	6.8	160	16	215	402	44	2000	0.87

Valkjärvi	4.4	0.15	7.0	15	6	18	86	12	68	0.51
Isojärvi	6.2	0.15	7.0	80	10	62	259	37	820	0.51
Valkea Kotinen	3.6	0.05	5.8	120	17	90	361	24	300	0.67
Hakojärvi	3.3	0.09	6.5	100	13	93	348	19	670	0.95
Iso Allasjärvi	4.4	0.05	5.9	180	26	271	392	74	2000	0.68
Mean	3.39	0.080	6.33	101	14.2	140.0	295.2	31.1	1083	0.601
Standard deviation	1.24	0.049	0.426	48.9	5.04	97.69	109.4	18.6	777.6	0.199
Reservoirs										
Kalajärvi	3.5	0.07	5.8	160	23	230	424	52	1400	1.51
Kyrkösjärvi	5.6	0.07	5.8	200	27	229	590	74	1600	1.61
Kivi- ja levalampi	2.9	0.00	5.4	150	28	197	516	47	790	1.80
Hirvijärvi	4.5	0.05	5.5	180	27	313	410	67	1700	1.40
Venetjärvi	2.9	0.00	5.6	180	18	188	335	32	780	1.28
Parana	5.0	0.04	6.0	220	20	255	196	60	1650	0.80
Hautaperä	7.7	0.15	6.8	200	22	237	479	64	1760	0.73
Uljua	3.5	0.10	6.6	240	20	291	396	64	2300	0.43
Lokka	2.0	0.07	6.7	140	13	119	196	41	600	0.42
Porttipahta	2.8	0.14	6.8	100	11	105	200	23	780	0.74
Mean	4.04	0.069	6.10	177	20.9	216.4	374.2	52.4	1336	1.07
Standard deviation	1.70	0.051	0.566	41.1	5.78	66.86	140.4	16.5	564.9	0.506

Fluorescence measurements (Aminco-Bowman spectrophotofluorometer) were made from diluted water samples (10x) to avoid concentration quenching (Pennanen and Mannio 1985).

The basic water chemistry measurements were made with methods used by the National Board of Waters (National Board of Waters 1981). The following analyses were used in the statistical treatments: oxygen saturation percentage (% O_2), suspended solids ($mg\ l^{-1}$), electrolytical conductivity ($mS\ m^{-1}$), alkalinity ($mmol\ l^{-1}$), pH value, colour (Pt $mg\ l^{-1}$), chemical oxygen demand ($COD_{Mn}\ mg\ l^{-1}\ O_2$), total nitrogen ($mg\ l^{-1}\ N$), total phosphorus ($\mu g\ l^{-1}\ P$), total iron ($\mu g\ l^{-1}\ Fe$), sodium ($mg\ l^{-1}\ Na$), potassium ($mg\ l^{-1}\ K$), magnesium ($mg\ l^{-1}\ Mg$), calcium ($mg\ l^{-1}\ Ca$) and silicic acid ($mg\ l^{-1}\ SiO_2$).

2.3 Pikes

Pikes were captured in the spring of 1983, 5 to 33 fish from each lake. Whole pikes were immediately frozen and stored at $-20^{\circ}C$. The analyses of total mercury of the muscle tissue under the dorsal fin were performed using a sodium hydroxide digestion procedure modified from that of Oda and Ingle (1981) (Surma-Aho et al. 1986). In the case of two lakes (Pihlajavesi and Kuorasjärvi) and one reservoir (Kivi- ja levalampi) with little data from 1983, previous measurements of mercury in pikes were available from the years 1980–82 and were included in this material.

The mean weight of the pikes was near to 750 g. Therefore the frequently used values for a »one kilogram pike» (Johnels et al. 1967) were not used. In this material the concentrations were calculated for 750 g pike by linear regression.

2.4 Statistical analysis

Correlation analysis (BMDP 8D) (Engelman 1981) and stepwise regression analysis (BMDP 2R) (Dixon and Jennrich 1983) were used to examine the relationships between the independent water quality parameters and the mercury content of pike. The stepwise regression analysis selected the variable most closely correlated with mercury content as the first independent variable in the equation and subsequently other variables

as long as the F-values of the variables in question were significant ($P < 0.05$). The equations were formed for lakes separately and for lakes and reservoirs together, both with stagnation and turnover water quality data. Due to the strong intercorrelation between the variables estimating humus concentration, only one such variable was included in each run.

3. RESULTS

3.1 Water quality

The water quality of the lakes and the reservoirs during autumn turnover is shown in Table 1. The variation of some of the parameters was as follows: pH 5.4–7.0, conductivity $1.7\text{--}7.7\ mS\ m^{-1}$, colour 10–240 Pt $mg\ l^{-1}$ and total phosphorus 7–74 $\mu g\ l^{-1}$. During winter stagnation (1 m depth) the pH range was from 5.1 to 6.7 and that of colour from 5 to 360 Pt $mg\ l^{-1}$. The oxygen saturation percentage varied between 12 and 100 % in winter.

3.2 Pikes

The correlation between pike mercury concentration and body weight was positive in all but three lakes and one reservoir and significant ($P < 0.05$) in 12 lakes and two reservoirs. The mercury concentration calculated for a 750 gram pike varied between $0.21\ mg\ kg^{-1}$ and $1.02\ mg\ kg^{-1}$ in natural lakes and between $0.42\ mg\ kg^{-1}$ and $1.80\ mg\ kg^{-1}$ in reservoirs (Table 1). When calculated for one kilogram pikes the values ranged between 0.25 and $1.90\ mg\ kg^{-1}$.

3.3 Correlation analysis

Pike mercury concentration was significantly correlated ($P < 0.001$) with all the variables describing the humic matter concentration of the water in lakes and reservoirs ($n=45$) during the autumn turnover. The best linear correlation was with chemical oxygen demand and UV-absorbance (Fig. 3a and b). Phosphorus and nitrogen were also correlated with mercury, probably

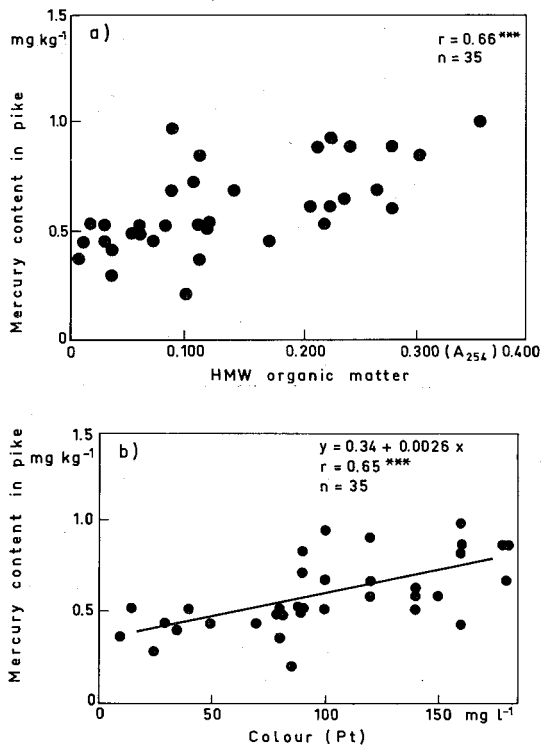


Fig. 2. The correlation between mercury content in 750 g pike and a) gel fractionated, optically measured high molecular weight organic matter and b) water colour in forest lakes ($n=35$).

due to the good correlation between nutrients and organic matter (Kortelainen et al. 1986). Significant correlation coefficients between mercury in pike (750 g) and water quality variables were in decreasing order:

COD	A254	LMW	F	COL	HMW	pH	P
0.70	0.63	0.59	0.57	0.54	0.52	-0.51	0.49
						($P < 0.001$)	
				N			
				0.44		($P < 0.01$)	

where

- COD = chemical oxygen demand (COD_{Mn}, O₂)
A254 = UV-absorbance (254 nm)
LMW = low molecular weight organic matter (see 2.2)
HMW = high molecular weight organic matter (see 2.2)
F = fluorescence (350/455 nm)
COL = colour of water (Pt)
pH = pH-value of water
P = total phosphorus
N = total nitrogen

In forest lakes ($n=35$) the best linear correlation was obtained with the HMW-fraction and colour (Fig. 2a and b). The correlation of iron with mercury in pike was also highly significant ($P < 0.001$) during the autumn overturn:

HMW	COL	A254	Fe	COD	F
0.66	0.65	0.63	0.56	0.55	0.53
				LMW	P
				0.51	0.49
					($P < 0.01$)

where

Fe = total iron

A slight difference between the HMW and LMW-fractions in relation to fish Hg concentration was observed in the autumn overturn data. In the natural lakes the parameters associated with the higher molecular weight organic matter (particulate + colloidal fraction, colour, iron) were pronounced in lakes with high pike Hg, whereas in reservoirs with high pike Hg the proportion of dissolved humic matter was greater (Fig. 4). During winter stagnation this difference was not observed:

COD	A254	COL	F	LMW	HMW	TOC	DOC
0.67	0.61	0.60	0.56	0.56	0.54	0.52	0.48
						($P < 0.001$)	
					pH	P	
					-0.42	0.41	($P < 0.01$)

where

TOC = total organic carbon

DOC = dissolved organic carbon

The winter stagnation data included some dilute samples from the epilimnion of strongly stratified lakes. These samples did not represent the conditions in the whole water body. Consequently the correlations between the stagnation water quality in lakes and mercury data were rather weak and only colour was correlated significantly with mercury ($r=0.46$, $P < 0.01$).

The pH of water did not correlate with pike Hg ($r < 0.20$) in the natural lakes alone, but when reservoirs were included the coefficient became significant ($P < 0.001$) (Fig. 3c). Lake Kangasjärvi, a clear (colour 5–10 Pt mg l⁻¹), acidic lake with low pike Hg (0.35 mg kg⁻¹), differed from all the other low pH-lakes, in which acidity was obviously more controlled by humic matter (Fig. 5a and b). Correlations of oxygen percentage, alkalinity, conductivity, Ca, Mg, K, Na, SiO₂ and suspended solids with pike Hg were not significant ($P < 0.01$) in any of the calculations.

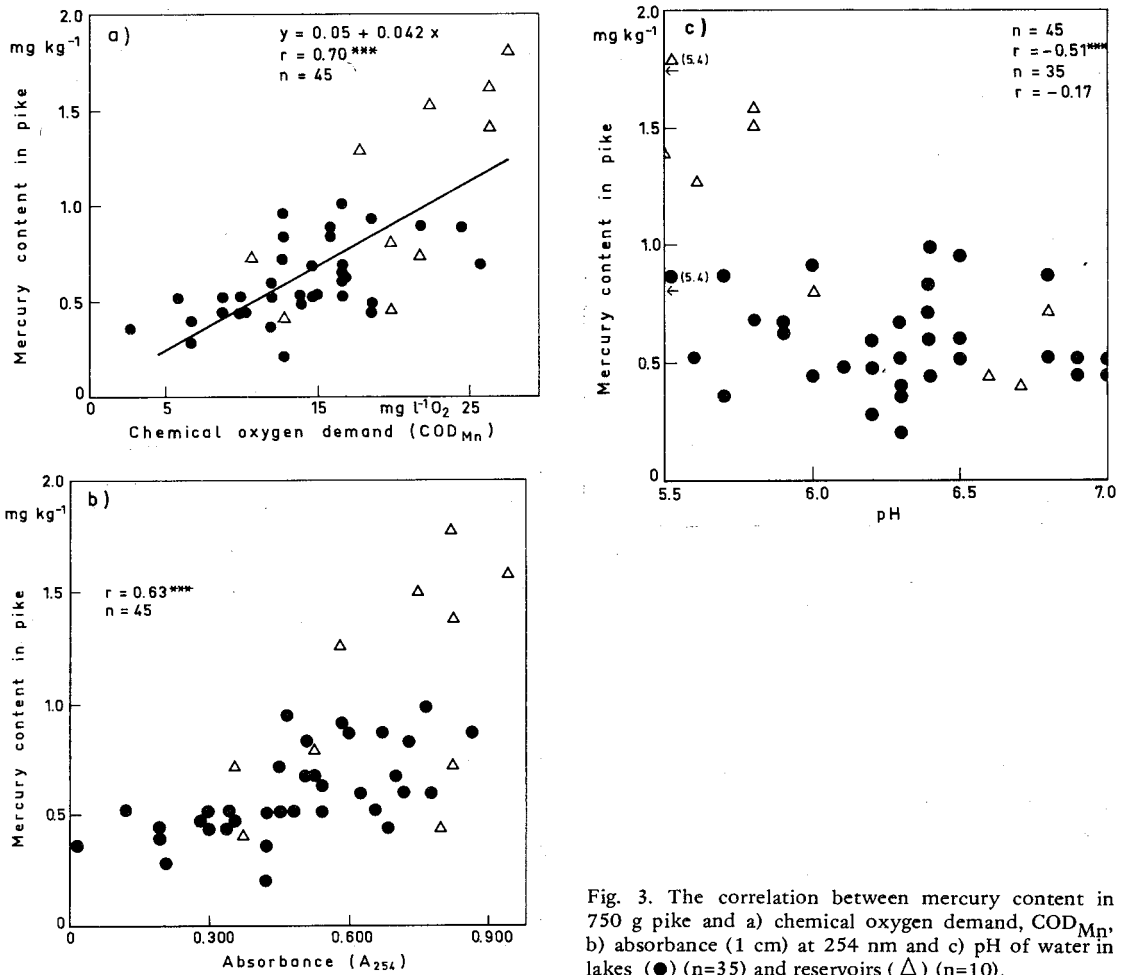


Fig. 3. The correlation between mercury content in 750 g pike and a) chemical oxygen demand, COD_{Mn} , b) absorbance (1 cm) at 254 nm and c) pH of water in lakes (●) ($n=35$) and reservoirs (Δ) ($n=10$).

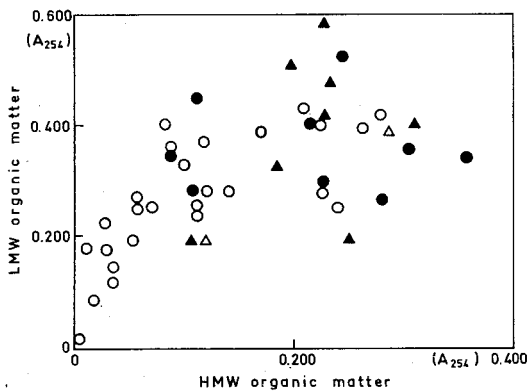


Fig. 4. Relation between high and low molecular weight humic matter during autumn overturn and the mercury content in 750 g pike in 35 forest lakes (O) $< 0.7 \text{ mg kg}^{-1}$ Hg (wet weight), (●) $> 0.7 \text{ mg kg}^{-1}$, and in 10 reservoirs (Δ) $< 0.7 \text{ mg kg}^{-1}$, (▲) $> 0.7 \text{ mg kg}^{-1}$.

3.4 Multiple regression analysis

The relative impact of different environmental factors on the mercury concentrations in pike was studied by stepwise regression analysis (BMDP 2R). The equations explained 21 to 56 % of the variance of the mercury concentrations in pike.

Lakes and reservoirs ($n=45$), autumn turnover

$$\text{Hg} = 0.052 \text{ COD} - 0.285 \log \text{SS} + 0.041 \quad r=0.75 \quad (1)$$

and without the humus parameters:

$$\text{Hg} = -0.315 \text{ pH} + 0.071 \text{ SiO}_2 + 0.4 \text{ N} + 2.17 \quad r=0.73 \quad (2)$$

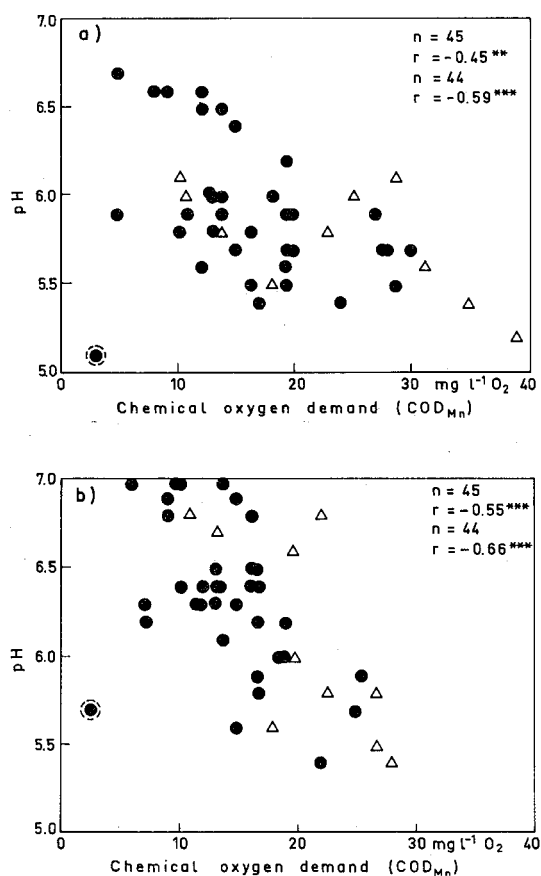


Fig. 5. The correlation between water pH and chemical oxygen demand in forest lakes and reservoirs ($n=45$) a) during winter stagnation and b) during autumn overturn (dotted circle is Lake Kangasjärvi).

Lakes and reservoirs ($n=45$), winter stagnation

$$\text{Hg} = 0.032 \text{ COD} - 1.37 \text{ alk} + 0.254 \quad r=0.72 \quad (3)$$

Lakes ($n=35$), autumn turnover

$$\text{Hg} = 1.3 \text{ HMW} + 0.031 \text{ SiO}_2 + 0.030 \text{ cond} + 0.264 \quad r=0.71 \quad (4)$$

$$\text{Hg} = 0.0026 \text{ colour} + 0.335 \quad r=0.65 \quad (5)$$

Lakes ($n=35$), winter stagnation

$$\text{Hg} = 0.0017 \text{ colour} + 0.402 \quad r=0.46 \quad (6)$$

where

Hg = mercury concentration in pike (750 g) (mg kg^{-1})

SS = suspended solids (mg l^{-1}) of water

COD = chemical oxygen demand (COD_{Mn} , $\text{mg l}^{-1} \text{O}_2$)

alk = alkalinity (mmol l^{-1})

HMW = high molecular weight organic matter (see 2.2)

cond = conductivity (mS m^{-1})

P = total phosphorus ($\mu\text{g l}^{-1}$)

N = total nitrogen (mg l^{-1})

SiO_2 = silicic acid (mg l^{-1})

colour = colour (Pt mg l^{-1})

4. DISCUSSION

4.1 The role of humus in pike mercury concentrations

Mercury has been shown to be very strongly bound to organic matter in soils (Andersson 1967, Cheam and Gamble 1974), sediments (Lindberg and Harris 1974, Miller 1975) and water (Strohal and Huljev 1971, Fitzgerald and Lyons 1973, Beneš et al. 1976). Binding occurs both in the low molecular weight fraction (Ramamoorthy and Kushner 1975, Andren and Harris 1975) and in the high molecular weight fraction (Beneš et al. 1976, Bowen et al. 1979, Lodenius et al. 1983). In laboratory studies both humic and fulvic acids have been shown to reduce (Alberts et al. 1974, Miller 1975, Skogerboe and Wilson 1980) and methylate mercury (Rogers 1977, Nagase et al. 1982) in a slightly acidic environment. These studies were carried out with inorganic mercuric salts. Reduction and abiological methylation appear to require inorganic mercury. However, in natural conditions, in which the ratio of mercury to humus is very low, almost all the mercury is assumed to be complexed to organic material (Andersson 1979).

The organic matter of the study lakes and reservoirs consisted mainly of humic material derived from the catchment area (Kortelainen et al. 1986). Although humic matter is rather slowly decomposed, its composition may change in watercourses due to sedimentation, reactions with inorganic substances and the effect of UV light. Gel fractionation gave an indication of the molecular distribution of humus in the water

column under two sets of conditions: the stable decomposition time in winter and the autumn turnover time with more autochthonic organic and allochthonic inorganic material in the water.

Of the chemical variables of water quality, all the estimates of humic matter correlated with pike mercury concentrations. The interpretation of the results is hampered by the very strong correlations between the explaining variables. The results of the multiple regression analysis confirmed the dominant role of humic matter. Other variables entering the equations could explain only a few percent more of the variation of mercury contents in pike.

In the case of natural forest lakes the high molecular weight fraction of organic matter (HMW) appeared to be the best single descriptor of pike mercury in the autumn overturn material (Fig. 2a). A possible explanation for this is that most of the high values of mercury in pike were recorded in the headwaters receiving »fresh» allochthonous humic matter straight from the nearby drainage area, or in chain lakes with short residence times, where the proportion of HMW-fraction was high. Iron may also affect the proportion of HMW (see 4.23 and Pennanen et al. 1986).

When lakes and reservoirs were examined together, the high content of mercury in pikes of the young reservoirs became apparent and affected the correlation coefficients. The organic matter of the young reservoirs appeared to contain most dissolved organic matter (LMW) (Kortelainen et al. 1986). Consequently, COD_{Mn} emerged as the best single independent variable describing pike mercury in forest lakes and reservoirs (Fig. 3a, equations 1,3).

Although it seems clear that humic matter acts as a carrier for mercury from the drainage area to the lake, it cannot be concluded on the basis of the gel fractionation data which specific properties of the humic material enhance the accumulation of mercury in biota. Verta et al. (1986b) reported a significant ($P < 0.01$) correlation between the terrestrial drainage area divided by lake volume (A/V) and pike mercury, but even more clear was the connection between this ratio and humus parameters ($P < 0.001$). These results indicate that the total input of humic matter from the drainage area could regulate the available mercury entering the food chain in lakes. In young reservoirs the source of the humic material and mercury is mainly the undated soil (Verta et al. 1986a).

4.2 The role of water quality parameters associated with humus concentration

4.21 pH

Suns et al. (1980) observed a relationship between the catchment area divided by lake volume (A/V) and mercury concentrations in yellow perch. They suggested that low pH may be a precondition in mercury accumulation and that the ratio (A/V) governs mercury availability. The pH was the only water quality parameter correlating with mercury.

In our material water pH was strongly related to organic matter (humic and fulvic acids) (Figs. 4a and b). The mercury entering a lake can be assumed mainly to be leached from the drainage area, or extracted from the inundated soil in reservoirs, and to be bound to humic material. Since low pH favours the formation of water-soluble monomethyl mercury (Fagerström and Jernelöv 1972), humus could contribute both directly and indirectly (by lowering the pH) to the availability of mercury in lakes.

4.22 Nutrients and suspended solids

Total nitrogen and total phosphorus were correlated in this material with mercury in pike, but even more with humus parameters (Kortelainen et al. 1986). In dystrophic lakes large amounts of P and N are bound to humic substances and are less available for primary production than in eutrophic lakes, in which higher production causes the mercury dilution effect to biomass and sedimentation removes mercury from the food chain. In addition, the higher pH of productive lakes favours the formation of volatile dimethyl mercury (Fagerström and Jernelöv 1972), Jernelöv et al. 1975, Beijer and Jernelöv 1979). Consequently, lower concentrations of mercury are expected in pikes in lakes with more nutrients. The correlation between nutrients and mercury in our material was undoubtedly apparent, due to the intercorrelation between the explaining variables. This phenomenon can also be seen in the multiple correlation analysis, where the omission of organic variables lead to the incorporation of variables clearly connected with the organic matter, although the multiple r^2 was almost unchanged (equations 1 and 2).

One parameter in our study could indicate the effect of sedimentation in scavenging available mercury. Suspended solids had a negative sign in

equation 1. Since humus is known to adsorb inorganic clayish material, suspended solids could act as a sink for humus containing mercury, especially during turnover periods.

4.23 Iron

The concentration of iron in water follows also the amount of humic matter. Lee et al. (1985) observed that iron could enhance the chemical methylation of mercury by humic substances under laboratory conditions. However, the laboratory experiments were carried out with inorganic mercury and iron. The actual effect of iron, which in polyhumic waters could already be complexed with humic matter, remains unclear. The association between iron and humic matter in natural waters is well documented (e.g. Shapiro 1964, Ghassemi and Christman 1968). The strong correlation between HMW and mercury in pike in natural lakes could have been influenced by iron, which is an important component of the HMW aquatic humus. The correlations of iron with HMW and LMW humus were 0.93 and 0.53, respectively (Kortelainen et al. 1986).

4.3 Conductivity, alkalinity and calcium

The bedrock in the study area consisted mainly of weathering-resistant granites, gneisses and granodiorites. These rocks import very poor buffering capacity to the surface waters. Consequently, the values of alkalinity, conductivity and major cations (Na, K, Ca, Mg) were low.

The overall low values and the narrow range (e.g. Ca 1.1–4.3 mg l⁻¹) of these parameters might explain the fact that they were not correlated with pike mercury concentrations. Wren and MacCrimmon (1983) found the lowest mercury levels in fish (Sunfish, *Lepomis gibbosus*) in lakes with the highest calcium concentrations, 14 to 22 mg l⁻¹ (range 2.0–22 mg l⁻¹). Pikes in Finnish lakes influenced by clayish soils in the drainage area are known to contain rather low levels of mercury (Verta et al. 1986b). Hultberg and Hasselrot (1981) reporting Swedish data concerning water quality and pike mercury concentrations, concluded that water pH had the greatest effect, whereas water colour and conductivity had much less influence.

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TIIVISTELMÄ

Ravinnon ja elinympäristön elohopeapitoisuuden ohella on kalojen elohopeapitoisuuteen todettu vaikuttavan mm. kalojen kasvunopeuden ja aineenvaihdunnan, veden kalsiumpitoisuuden, alkaliteetin, pH:n, ravinnetasen ja humusaineiden. Kohonneita elohopeapitoisuuksia on tavattu myös ns. luonnontilaisten vesien kaloissa.

Tässä tutkimuksessa pyrittiin selvittämään, mitkä vedenlaatutekijät selittävät parhaiten haiden elohopeapitoisuuksia latvavesistöissä ja tekoaltaissa, joihin ei tule suoraa elohopeakuormitusta teollisuudesta, asutuksesta eikä maataloudesta.

Järvet (35 kpl) sijaitsivat lähinnä Suomenselän vedenjakajaseudulla ja tekoaltaat (10 kpl) Pohjanmaalla ja Lapissa. Veden pH-luku syystäyskierron aikana oli 5,4–7,0, sähköjohtavuus 1,7–7,7 mS m⁻¹, väriluku 10–270 Pt mg l⁻¹ ja kokonaisfosfori 7–74 µg l⁻¹. Haukien (750 g) elohopeapitoisuustaso oli metsäjärvisissä 0,21–1,02 mg kg⁻¹ ja tekoaltaissa 0,42–1,80 mg kg⁻¹.

Vedenlaadun ja haiden elohopeapitoisuuden välistä yhteyttä tutkittiin tilastollisesti korrelaatio- ja monimuuttujaregressioanalyysillä. Kaikki orgaanista ainetta, näissä järvisä lähinnä humusta, kuvaavat muuttujat korreloivat merkitsevästi tai erittäin merkitsevästi haiden elohopeapitoisuuden kanssa. Myös elohopean korrelaatio ravinteisiin ja rautaan oli positiivinen, mikä tässä aineistossa ilmensi näiden aineiden pitoisuuksien kytkeytyvän humukseen. Monimuuttujayhtälöt selittivät parhaimmillaan 56 % haiden elohopeapitoisuuden vaihtelusta, mutta orgaanisen aineen kuvaajat yksinkin noin 40–49 %. Tekoaltaissa

alhaisella pH-luvulla näytti olevan selvempi yhteys korkeisiin pitoisuuksiin kuin metsäjärvisssä. Alkaliteetilla, sähköjohtavuudella ja emäskatio-neilla (Na, K, Ca, Mg) ei havaittu olevan yhteyttä elohopeapitoisuuksiin.

Vaikka humus näyttää selvästi toimivan elohopean kuljettajana valuma-alueelta vesistöön, ei geelifraktioinnin perusteella voida päätellä, mitkä humuksen ominaisuudet vaikuttavat elohopean kertymiseen eliöihin. Tutkimus tukee käsitystä, että suuren terrestrisen valuma-alueen aiheuttama kokonaishumuskuormitus säätelee ravintoketjuihin siirtyvää elohopeaa. Nuorissa tekoaltaissa li-säksi veden alle jääneestä maaperästä uuttuu huomattavasti humusta ja siihen sitoutunutta elohopeaa.

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